RESEARCH PROPOSAL

COMPUTATIONAL STUDY OF STRUCTURAL AND ELECTRONIC PROPERTIES OF CERTAIN LAYERED MATERIALS

For Registration to the Degree of

Doctor of Philosophy

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1. Introduction

Materials can be classified according to their mechanical (flow) behavior. The solids are the materials whose shear viscosities exceed $10^{14.6}$ poise while fluids have shear viscosities of less than $10^{14.6}$ poise. Solids can be characterized into two categories; *crystalline and non-crystalline or amorphous solids*.

A crystal is a regular three dimensional design and is a consequence of the regular arrangement of the atoms, molecules or of ions in a sea of free electrons, of which it is built-up. When this periodicity extends throughout a certain piece of material, one calls it a *single crystal*. A *polycrystalline material* is composed of tiny crystals.

The periodicity of the structure in the polycrystalline materials is interrupted at the so called grain boundaries. The size of grains in which the structure is periodic may vary from microscopic dimensions to a size much larger as compared to the pattern unit size.

When the size of the grains or the crystallites become comparable to the size of the pattern unit, one can no longer speak of crystals since the essential feature of the crystalline material i.e., the periodicity of the structure is missing, one then speaks of non-crystalline, amorphous, glassy or vitreous solid. A comparison of Crystalline and amorphous materials is given below in Table 1.

Table 1: Comparison of characteristic feature of crystalline and amorphous materials

Crystalline Solids	**Amorphous Solids**
Crystals have a specific geometric shape with definite edges.	Amorphous solids have no geometry in their shapes.
Crystalline solids have a sharp melting point on which they will definitely melt.	An amorphous solid will have a range of temperature over which it will melt, but no definite temperature as such.
Crystals have a long order arrangement of their particles. This means the particles will show the same arrangement indefinitely.	Amorphous solids have a short order arrangement. Their particles may show a lot of varieties in their arrangement.

Crystalline materials

Crystalline materials are those which have the atoms or molecules arranged in regular and periodic manner in three dimensional structure. Each atom or molecule in its equilibrium is fixed at finite distance from surrounding atoms or molecules. There is also a definite angular orientation to all other atoms surrounding it. Crystalline materials are anisotropic. These materials melt at a definite temperature, so they possess a sharp melting point. Crystalline solids have their atoms arranged in three dimensional space in basic forms, called lattices – *Bravais lattices.*
There are basically 7 lattice systems, namely, *Cubic, hexagonal, tetragonal, orthorhombic, rhombohedral, monoclinic, and triclinic.*

Crystal structures of commonly used metals and alloys can be grouped into three types, namely, body centered cubic **[BCC],** face centered cubic **[FCC]** and hexagonal close-packed **[HCP].** The smallest group of stacked atoms which repeats itself in three dimensional spaces and hence fixes the lattice structure, can be defined as unit cell.

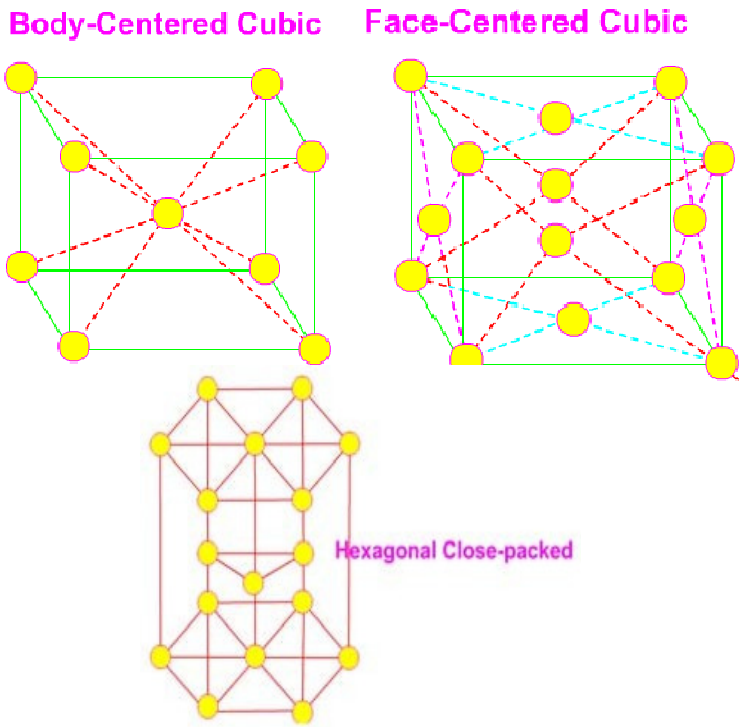


Fig. 1: Unit cell structures of Cubic and HCP lattices

Physical and mechanical characteristics of crystalline solids are dependent on the effective number of atoms in a unit cell, density and orientation of packing of atoms within the unit cell. Unit cells are represented by hard-ball models. The effective number of atoms in a unit cell represents the extent of packing of atoms and void space within the unit cell.

Crystal imperfections:

Crystal structures are never perfect – there are defects in the arrangements of atoms in crystalline materials. Imperfections arise during growth of crystals or solidification of crystalline materials, or they may occur during processing of material like mechanical deformation. Adding alloying element is a deliberately introduced imperfection.
There are *three* types of defects which generally occur in crystals, namely, *point defects, line defects and surface defects.* Other defects observed in crystals are follows:

Vacancy – Missing of an atom from a lattice position. It can happen due to nuclear irradiation of a material.
Interstitial defect – Presence of an additional atom in the interstitial space.
Frenkel defect – Ion removed from its regular position and moved to interstitial position.
Schottky defect – Missing pair of ions of opposite charge.

Categorization of crystals on the basis of Conductivity:

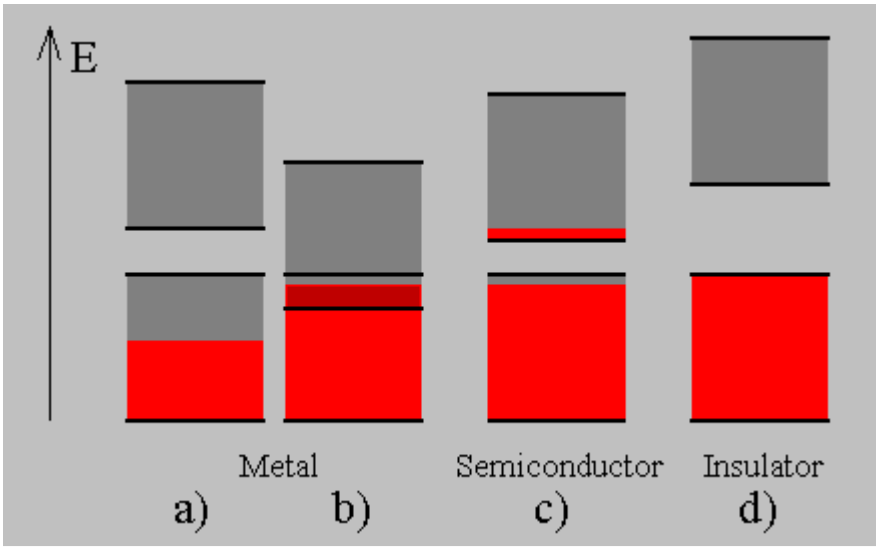
Every solid has its own characteristic energy band structure. For a material to be conductive, both free electrons and empty states must be available. Whereas free electrons reside in conduction band states, the empty states occur in valence band called as holes.

Metals have free electrons and partially filled valence bands, therefore they are highly conductive (a). Examples: Na, K, Al, Cu, Ag, Au etc.

Semimetals have their highest band filled. This filled band, however, overlaps with the next higher empty band, therefore they are partially conductive and show higher resistivity than normal metals (b). Examples: arsenic, bismuth, antimony etc.

Semiconductors have similar band structure as insulators but with a much smaller band gap. Some electrons can jump to the empty conduction band by thermal or optical excitation (c). E_g=1.1 eV for Si, 0.67 eV for Ge and 1.43 eV for GaAs.

Insulators have filled valence bands and empty conduction bands, separated by a large band gap E_g(typically >4eV), they have high resistivity(d). Examples: Diamond, Graphite, air, oil, plastic etc.



Nanomaterials :

Nanomaterials describe, in principle, the materials of which a single unit is sized (in at least one dimension) between 1 to 1000 nanometres (10^{-9} meter) but usually taken as 1 to 100 nm.

Classification of nanomaterials:

Typically, nanoparticles (**NPs**) are defined as an agglomeration of atoms and molecules in the range of 1–100 nm. They can be composed of one or more species of atoms (or molecules) and can exhibit a wide range of size-dependent properties. Within this size range, NPs bridge the gap between small molecules and bulk materials in terms of energy states. NPs are generally classified on the basis of their dimensionality, morphology, composition, uniformity and agglomeration.

a) Dimensionality

1D nanomaterials: Materials with one dimension in the nanometre scale are typically thin films or surface coatings. Thin films have been developed and used for decades in various fields including electronics, information storage systems, chemical and biological sensors, fibre-optic systems, and magneto-optic and optical devices. Thin films can be deposited by various methods and can be grown controllably at the atomic level (a monolayer).

2D nanomaterials: 2D nanomaterials have two dimensions in the nanometre scale These include for example, nanotubes, dendrimers, nanowires, fibres and fibrils. Free particles with a large aspect ratio with dimensions in the nanoscale range are also

considered to be 2D nanomaterials. The properties of 2D systems are less well understood and their manufacturing capabilities are less advanced.

3D nanomaterials: Materials that are nanoscale in all three dimensions are considered to be 3D nanomaterials. These include quantum dots or nanocrystals, fullerenes, particles, precipitates and colloids. Some 3D systems, such as natural nanomaterials and combustion products, metallic oxides, carbon black, titanium oxide (TiO_2) and zinc oxide (ZnO) are well known, while others such as fullerenes, dendrimers and quantum dots represent the greatest challenges in terms of production and understanding of properties.

b) The morphology of NPs and nanocomposites

The morphological characteristics to be taken into account are the flatness, aspect ratio and spatial position of each element in the case of hybrid NPs (HNPs). A general classification exists between high and low aspect ratio particles. High aspect ratio NPs include nanotubes and nanowires. Small aspect ratio morphologies include spherical, oval, cubic, prism, helical and pillar shapes.

c) Chemical composition

NPs can be composed of a single constituent material or be a composite of several materials. The NPs found in nature are often agglomerations of materials with various compositions, while pure single-composition materials can be easily synthesized using a variety of methods .There are three main types of chemical ordering in HNPs that describe the way in which the atoms of the elements are arranged within the same NP: Mixed NPs can be either random or ordered. Randomly mixed alloys correspond to solutions of solids, whereas an ordered binary nanoalloy may correspond to ordered arrangement of A and B atoms.

Core–shell NPs consist of a shell of one type of atom say (B) surrounding a core of another type of atom say (A) This pattern is generally denoted by A-B and is common for a large class of NPs. Various thermodynamic considerations , lead to the segregation of materials within the core or shell. A subset of the core–shell category consists of multishell (or 'onion-like') NPs. These NPs have alternating A–B–A shells, or arranged in a pattern like A–B–C in the case of ternary NPs.

Layered NPs are commonly referred to in the literature as Janus (or 'dumbbell like') NPs. They consist of two types of NPs (A and B), sharing a common interface. These types of NPs tend to minimize the number of bonds between elements A and B. This heterojunction structure facilitates phase separation.

d) Uniformity and agglomeration

Based on their chemistry and electromagnetic properties, NPs can exist as dispersed aerosols, suspensions/colloids or in an agglomerate state. In fact, NPs tend to adhere to each other and to form agglomerates because of van der Waals forces that act over short distances, magnetic interactions, electrostatic forces present in the particles and adhesion forces related to the liquids adsorbed on their surfaces. Nanoparticles research is gaining increasing interest due to their unique properties, such as, increased electrical conductivity, toughness and ductility, increased hardness and strength of metals and alloys, luminescent efficiency of semiconductors and formability of ceramics etc.

The successful isolation of *graphene* in 2004 has attracted great interest to search for potential applications of this unique material and other members of the two-dimensional materials family in electronics, optoelectronics and their interface with the biological systems. At this early stage of 2D materials research, many opportunities and challenges co-exist in this area. It has been more than a decade since the first electrical characterization of graphene, a material consisting of a single layer of sp^2 -bonded carbon atoms arranged in a honeycomb lattice, was done. Thought to be an impossible goal for many decades, its successful isolation in 2004 not only led to intensive research by physicists and chemists but also inspired renewed interest in carbon based electronics for device engineers and circuit designers around the world.
Rapid progress has been made in the past few years to develop applications for graphene. Many interesting ideas have been demonstrated in the laboratory setting and some attractive products may emerge at the industrial scale in the coming years. Some of the promising applications include RF electronics, advanced sensors, semi-transparent electrodes and electronics, low power switches, solar cells, battery energy storage, and tunable plasmonic devices for THz and mid-infrared applications. In addition to its unique properties, it should be highlighted that graphene is only the beginning of an emerging 2D materials family. 2D materials, such as molybdenum disulfide (MoS_2) and other members of the transition metal dichalcogenides family, represent the ultimate scaling of the material's dimension in the vertical direction. Nano-electronic devices built on 2D materials offer many benefits for further miniaturization following Moore's Law and as a high-mobility option in the rising field of large-area and low-cost electronics that is currently dominated by low-mobility amorphous silicon and organic semiconductors.
MoS_2, a 2D semiconductor material, is also attractive as a potential complement to graphene for constructing digital circuits on flexible and transparent substrates, while its bandgap of the order of 1.8 eV, as measured by photoluminescence, and potentially even a higher electronic band gap due to the excitonic energy, is advantageous over silicon for suppressing the source-to-drain tunneling at the scaling limit of transistors.

The unique properties of 2D materials have attracted intense research activities to take advantage of this new material system for improving existing electronic, optoelectronic and sensing applications and inventing new ones.

Layered Materials

Layered materials with a large anisotropy to their bonding, and varied electrical and/or magnetic properties, have been important in the development of solid state chemistry, physics and engineering applications.
Layered materials were the initial test bed where chemists developed intercalation chemistry that evolved into the field of top chemical reactions, where researchers are able to perform sequential steps to arrive at kinetically stable products that cannot be directly prepared by other approaches. Physicists have used layered compounds to discover and understand novel phenomena, made more apparent through reduced dimensionality. The discovery of charge and spin density waves and more recently their markable discovery in condensed matter physics of the two-dimensional topological insulating states, were discovered in two-dimensional materials. The understanding developed in two-dimensional materials enabled subsequent extension of these and other phenomena into three-dimensional materials.

Layered compounds have also been used in many technological applications as engineers and scientists used their unique properties to solve challenging technical problems (low temperature ion conduction for batteries, easy shear planes for lubrication in vacuum, edge decorated catalyst sites for catalytic removal of sulfur from oil, etc.).

2D Materials, sometimes referred to as single layer materials, (but way better self-description title is "topological materials", as not every such material is purely "2D", or monolayered, but there are also such other materials, for example, various nanotubes (buckminster, fullerenes, etc..),which are crystalline, consisting of a single layer of atoms. These materials have found use in various applications such as photovoltaics, semiconductors, electrodes and water purification.
The first 2D material, *graphene*, a single layer of graphite, was isolated in 2004. Thereafter many other 2D materials have been identified.

Table 2: Comparison of properties of Graphite and Graphene

Graphite(Bulk)	Graphene(Monolayer)
Graphite is a commonly found mineral and is composed of many layers of graphene.	Graphene is simply one atomic layer of graphite - a layer of sp^2 bonded carbon atoms arranged in a hexagonal or honeycomb lattice.
Graphite is naturally a very brittle compound and cannot be used as a structural material on its own due to its *sheer planes* (although it is often used to reinforce steel).	Graphene, on the other hand, is the strongest material ever recorded, more than three hundred times stronger than A36 structural steel, at 130 gigapascals, and more than forty times stronger than diamond.
Due to graphite's planar structure, its thermal, acoustic and electronic properties are highly anisotropic, meaning that phonons travel much more easily along the planes than they do when attempting to travel through the planes.	Graphene, on the other hand, being a single layer of atoms and having very high electron mobility, offers fantastic levels of electronic conduction due to the occurrence of a free pi (π) electron for each carbon atom.

1.1 What are 2D Materials?

The most commonly-studied 2D materials are graphene and Group VI (molybdenum and tungsten) *transition metal dichalcogenides*. They are both characterized both by a layer of in-plane, covalently-bonded atoms, and weak out-of-plane van der Waals coupling between adjacent layers (see Figure 2).

In the case of graphene, the carbon atoms in single-atom-thick layer of are arranged in a hexagonal structure, held together by strong sp^2 covalent bonding. This structure leads to monolayer graphene's superior properties; namely, it has been shown to be the strongest material ever measured (10 times stronger than steel), more conductive than silver, and possesses highly mobile charge carriers that behave like massless Dirac fermions due to its linear dispersion at low energies.

Once graphene transitions from monolayer to bilayer and to a few layers, the bandstructure and, thus, the properties change in a recurring theme in this field.

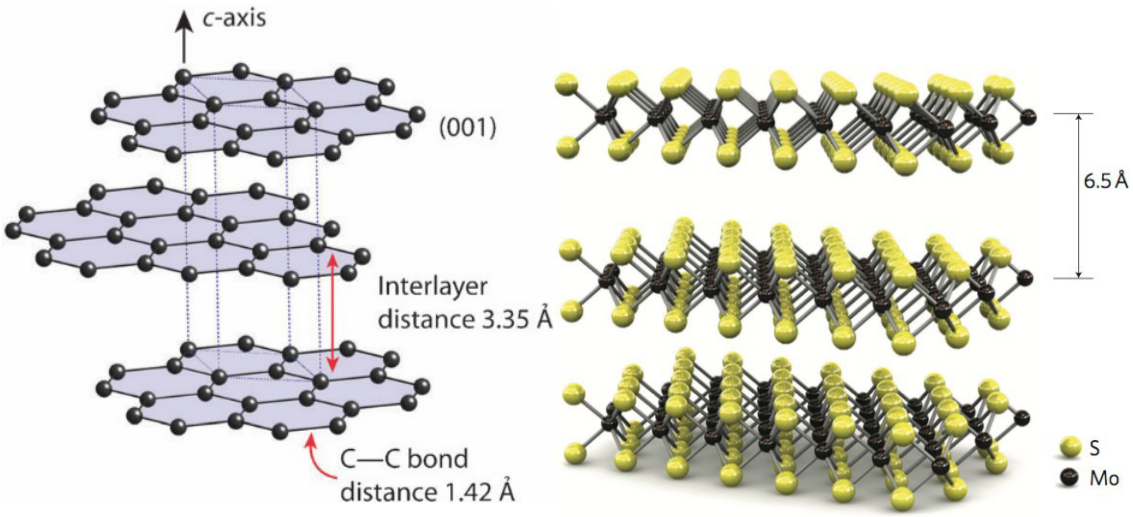


Figure 2. Ball and stick model for 3-layergraphene (left) and 3-layer MoS_2(right). (Left)Single-layer grapheme is held together by in-plane covalent sp^2 carbon-carbon bonds. The interlayer separations are 3.35 Angstroms. (Right)Single-layer MoS_2 has a center plane of trigonally- coordinated molybdenum atoms that are each bonded to 2 sulfur atoms above and below the plane. The interlayer separation is 6.5 Angstroms.

Group VI transition metal dichalcogenides, however, exhibit multiple structures, with different levels of stability, in just the X-M-X (chalcogen-transition metal-chalcogen) monolayer: hexagonal (2H), octahedral (1T), and distorted octahedral (1T') (see Figure 2) **MoS_2**, **$MoSe_2$**, **WS_2**, and **WSe_2** are most stable in the hexagonal phase, which is semiconducting. This has been explored as a possible route to forming low-resistance electrical contacts to the semiconducting hexagonal phase with varying levels of success as well as a potential new material system for non-volatile memory applications.

However, at room temperature, these phases are very unstable and thus difficult to control and spatially manipulate. Another Group VI Transition Metal Dichalcogenides (**TMDC**), $MoTe_2$, is also most stable in the hexagonal phase at room temperature; however, it's monoclinic 1T' phase is metastable at room temperatures. WTe_2 is the largest departure from its Group VI counterparts, as its room temperature phase is the semi-metallic, distorted octahedral phase (called 1T" due to its orthorhombic crystal structure).

Why are they Interesting?

In general, the term "2D materials" is actually quite vague as there is a wide collection of materials that fall into this class with a broad range of properties. There are layered insulators, semimetals, small and moderate band gap semiconductors. There are layered materials, such as black phosphorus and ReS_2, that exhibit in-plane optical and electrical anisotropy. The 2H diatomic crystals, such as h-BN and MoS_2, possess nonzero piezoelectric coefficients in odd-numbered layers. The only common thread amongst them all is that they possess strong covalent intralayer bonding with weak van der Waals interlayer coupling. This common thread simply means that the weak interlayer forces allow these bulk materials to be mechanically-exfoliated onto a substrate, isolating as few as one single monolayer, and so many of the techniques that were developed initially for the study of graphene can be, and have been, employed in these material systems. However, given that there are a wide range of properties exhibited by these materials, it is useful to outline some of the more noteworthy properties in order to isolate particular areas where they may be able to close an existing technology gap:

Superior elastic properties:

- Strength and stiffness.
- Ultra-thin and flexible.
- Trap-free interfaces.
- Amenable to heterostructures.
- Strong light-matter interactions.

Elastic properties: Initial excitement over the elastic properties of 2D materials began with the early work of Lee, Kysar and Hone et al. (2008). Their nano indentation experiments measured the intrinsic elastic properties of free-standing graphene membranes prepared by mechanical exfoliation of natural graphite crystals. This work reported an effective Young's modulus of 1 TPa and an intrinsic breaking strength of 130 GPa at a strain of 25%. Follow-up studies on graphene grown in large areas by chemical vapor deposition showed that grain boundaries that were still well-stitched were not significantly weaker than the pristine material. Similar experiments performed on single domains of exfoliated and CVD-grown MoS_2 reported effective Young's moduli of 210 GPa and 264 GPa, respectively, with a breaking strength of 27 GPa at a strain of approximately 23%. While notably weaker and less stiff than graphene, it is still quite remarkable for a 2D crystal. The remarkably high stiffness has motivated pursuits of tunable membrane resonators that operate at MHz frequencies. The strain limits have motivated the integration of these materials into flexible electronics.

Flexibility: One of the application where 2D materials probably hold the most promise is in flexible electronics. With in-plane strain limits of the order of 20%, they exceed the limits of conventional electronic materials.

Trap-free Interfaces: Another potential application of 2D materials is in tunnel field-effect transistors (**TFETs**). TFETs are a potential low-power replacement to conventional transistors. They rely on quantum mechanical band-to-band tunneling instead of thermionic emission over a gate-modulated barrier in order to overcome the thermodynamic limits that plague conventional transistors. This would allow the transistors to be switched on and off faster while dissipating less power. One impediment that limits conventional materials is the formation of interface traps between dissimilar materials that arise from lattice mismatches as well as the fact that 3D materials inherently have bonds out-of-plane.

Heterostructures: A trend in 2D materials research has been towards the formation of heterostructure architectures. There are several reasons for this: Improving carrier transport by isolating the channel from disorder and surface polar phonons that are ever present in oxide dielectrics. This initally began with report from Wang et al.(2014) that demonstrated drastically improved performance in the electronic properties of graphene when using a layered h-BN.

Strong Light-Matter Interactions: One of the most remarkable properties of some of these 2D semiconductors are the extremely strong light matter interactions they exhibit. The Group VI TMDCs absorb nearly 10% of incident photons in the visible range .There are, of course, strong resonances at the direct optical transitions.

1.2. Basic Interactions in many electron systems

Materials are made up of atoms and atoms are made up of nuclei and electrons. In metals some of the atomic electrons become free and form an electronic sea, in which ions or molecules move. The free electrons also provide a cohesive media for ions or molecules to adhere; with the result the ions/atoms/molecules form what we call a lattice. While ions/atoms/molecules forming the lattice vibrate about their mean positions, the free electrons move through the lattice. Motion of electrons in atoms or molecules is described by the electronic structure theory. From the Born-Oppenheimer approximation, electrons are so much lighter than nuclei that they will find their optimal

distribution for any given configuration of ions/atoms/molecules. Solving the electronic problem for a range of nuclear configuration gives potential energy surface. Electrons are too small; hence we need quantum mechanics to study their motion. According to quantum mechanics, electrons will not be localized at particular points in space, but they are best thought of as matter waves. The probability of finding a single electron at a given point is given by $\psi^*(x)\psi(x)$ for any wavefunction ψ at the point x.
We can determine wavefunction by solving the time independent Schrodinger equation $H\psi = E\psi$. We solve non relativistic electronic Schrodinger equation keeping nuclei fixed under Born-Oppenheimer approximation

$$\hat{H} = -\frac{\hbar^2}{2m}\sum_i \nabla_i^2 - \sum_A \frac{\hbar^2}{2M_A}\nabla_A^2 - \sum_{A,i}\frac{Z_A e^2}{4\pi\epsilon_0 r_{Ai}} + \sum_{A>B}\frac{Z_A Z_B e^2}{4\pi\epsilon_0 R_{AB}} + \sum_{i>j}\frac{e^2}{4\pi\epsilon_0 r_{ij}} \quad - \quad \mathbf{(1)}$$

In atomic units (when e=m=ħ=1 and $\frac{1}{4\pi\varepsilon}$ =1)
Where i, j refer to electrons and A,B refer to nuclei. This simplifies to

$$\hat{H} = -\frac{1}{2}\sum_i \nabla_i^2 - \sum_A \frac{1}{2M_A}\nabla_A^2 - \sum_{A,i}\frac{Z_A}{r_{Ai}} + \sum_{A>B}\frac{Z_A Z_B}{R_{AB}} + \sum_{i>j}\frac{1}{r_{ij}} \quad - \quad \mathbf{(2)}$$

In this expression, the first term corresponds to Kinetic Energy of electrons, second to the kinetic energy of nuclei, third to the interactions between electrons and nuclei of same atom, fourth to the interaction between different nuclei and the last term corresponds to interactions between different free electrons in the nuclei of metal. The Hamiltonian is applicable if we do not consider relativistic effects for the system. In general, relativistic effects are not considered for atoms with atomic number less than 25 (Mn). For heavier atoms, inner electrons are held tightly to the nucleus and their velocities increase with atomic number. As these velocities reach closer to the speed of light, relativistic effects become more important. To solve the Schrodinger equation for materials having large number of atoms using the DFT, it is necessary to understand certain approximations of the Schrodinger equation. There are large number of model Hamiltonians which are in use, such as Huckel, tight binding model, the Hubbard and Heisenberg Hamiltonians, the BCS model. For finite systems, simple method is the configuration interaction method Zeiss *et al.*(1983).

1.2.1 The Born-Oppenheimer Approximation

The forces on electrons and nuclei are of the same order and hence suggesting momenta of same magnitudes. In this case electrons move comparatively more rapidly than nucleus due to smaller mass. Hence, one can assume that the electrons in a molecule adjust instantaneously to a given configuration of the nuclei. This means the electrons follow the nuclear motion while remaining in the instantaneous ground state of the

electronic Hamiltonian. The Born-Oppenheimer approximation for fixed set of coordinates R = {R_I} is given by,

$$H_R^{BO}\psi_R = (H_{ee} + H_{ne} + H_{nn})\psi_R = \left(-\frac{\hbar^2}{2m_e}\sum_i \frac{\partial^2}{\partial r_i^2} + V_{ne} + V_{ee} + V_{nn}\right)\psi_R \quad \text{- (3)}$$
$$= E_R\psi_R$$

Where ψ_R is a function of the electronic coordinates and depends parametrically on the nuclear coordinates R. The kinetic energy of the nuclei is not considered due to the very heavy mass of nuclei and hence very high nuclear to electronic mass-ratio. The term V_{nn} can also be dropped from the Eq. (3), as it results in a trivial shift in the energy, i.e, it is not germane to the problem of describing the electrons due to its being constant for a fixed nuclear configuration.

The resulting separation of the states among electronic and nuclear degrees of freedom is a very useful simplification of the problem and allows one to treat the nuclei within a classical framework. The electronic part is still a quantum many body problem; the electronic wavefunction of the system depends on the coordinates of all the electrons and cannot be decoupled in single- electron contributions because of their mutual interaction. This makes the solution complex as it requires the solution of a coupled differential equation of $3N_e$ and N_e spatial and spins variables respectively. For atoms the number of electrons is in the range $N_e \sim$ 1-100. However, the small molecules have often more than 100 electrons, while for a solid $N_e \sim 10^{23}$. Hence, the problem is still too complicated to be solved in practical computations suggesting further simplifications.

1.2.2 The Hartree-Fock Theory

A many-electron wave function may be constructed from a set of orthonormal one-electron orbitals in the form of a *Slater determinant*:

$$\psi_{HF}(\{x_i\}) = \frac{1}{\sqrt{N!}}\begin{vmatrix} \phi_1(x_1) & \phi_1(x_2) & \ldots \phi_1(x_n) \\ \phi_2(x_1) & \phi_2(x_2) & \ldots \phi_2(x_n) \\ & \vdots & \\ \phi_n(x_1) & \phi_n(x_2) & \ldots \phi_n(x_n) \end{vmatrix}. \quad \text{- (4)}$$

The Hartree–Fock method often assumes that the exact, N-body wave function of the system can be approximated by a single Slater determinant (in the case where the particles are fermions) or by a single permanent (in the case of bosons) of N spin-orbitals. By invoking the variational method, one can derive a set of N-coupled equations for the N spin orbitals. A solution of these equations yields the Hartree–Fock wave function and energy of the system.

Especially in the older literature, the Hartree–Fock method is also called the self-consistent field (**SCF**) method. In deriving what is now called the Hartree equation as an approximate solution of the Schrodinger equation, Hartree required the final field as computed from the charge distribution to be "self-consistent" with the assumed initial field. Thus, self-consistency was a requirement of the solution. The solutions to the non-linear, Hartree–Fock equations also behave as if each particle is subjected to the mean field created by all other particles and hence, the terminology continued. The equations are almost universally solved by means of an iterative method; although the fixed-point iteration algorithm does not always converge. This solution scheme is not the only one possible and is not an essential feature of the Hartree–Fock method.

1.2.3. Density Functional Theory

- Density Functional Theory (**DFT**) proposed by Kohn *et al.* (1965) is now the dominant method for the quantum mechanical simulation of periodic system.
- Rather than working with particle wavefunctions, it is based on density of particles.
- DFT gets information about the energy, structure and the molecular properties of molecules based on the wavefunctions.
- It reduces 3N dimensional wave function into 3 dimensional functionals based on electron density wave functions.
- In DFT the functional of the electron density is a function of space and time.
- By focusing on electron density it is possible to derive an effective one electron type Schrodinger equation.

Thomas Fermi Dirac Approximation

- In Thomas Fermi method the kinetic energy of the system of electrons is approximated as an explicit functional of the density.
- Thomas and Fermi neglected exchange and correlation energy.
- Electron experiences a potential field generated by the nuclear charge and by electron distribution itself.
- It applies on an inhomogeneous situation as that of atoms, metals and solids.

The Hohenberg-Kohn Theorem:

Hohenberg and Kohn(1964) introduced two theorems:-
Theorem 1: For any system of interacting particles in an external potential V_{eff}(r) there is a unique ground state density.

Theorem 2: There exist a universal functional for energy E[n] in terms of the density n(r) such that the ground state energy is minimized at the ground state density.

1.2.3.1. Kohn-Sham Equations

Kohn and Sham(1965) takes two assumptions, which are:-

- The exact ground state density of a system of interacting particles can be represented by the ground state density of an auxiliary system of non-interacting particles. This is called "non-interacting-V representability".
- The auxiliary Hamiltonian is chosen to have the usual kinetic energy operator and an effective local potential $V_{eff}^{\sigma}(r)$, acting on an electron of spin σ at point r.

Self Consistent Loop

The Self Consistent solution of Schrodinger equation under DFT can be understood by the following flow chart.

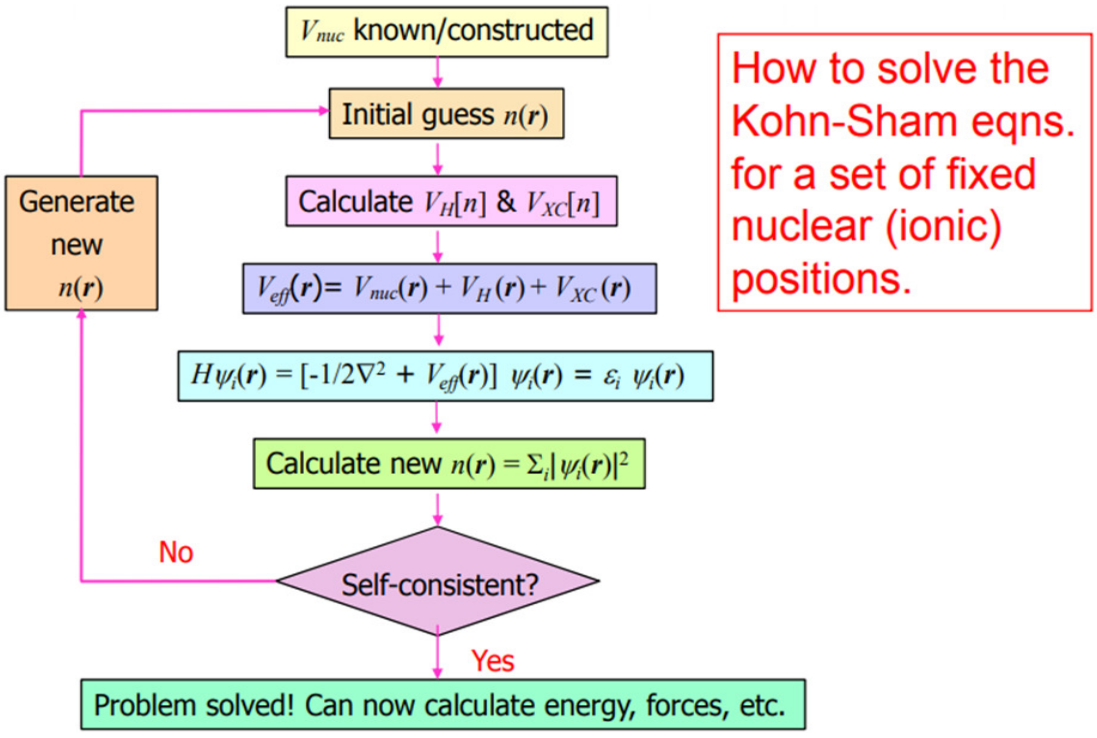

V_{nuc} known/constructed
Initial guess $n(r)$
Calculate $V_H[n]$ & $V_{XC}[n]$
$V_{eff}(r) = V_{nuc}(r) + V_H(r) + V_{XC}(r)$
$H\psi_i(r) = [-1/2\nabla^2 + V_{eff}(r)]\ \psi_i(r) = \varepsilon_i\ \psi_i(r)$
Calculate new $n(r) = \Sigma_i|\psi_i(r)|^2$
Self-consistent?
No
Yes
Generate new $n(r)$
Problem solved! Can now calculate energy, forces, etc.
How to solve the Kohn-Sham eqns. for a set of fixed nuclear (ionic) positions.

Fig. 3: Flow chart showing self consistent solution of Schrodinger equation under DFT

1.2.3.2. Local Density Approximation

- The LDA approximation assumes that the particle density is a slowly varying function and the inhomogeneous density of particles in a solid or molecule can be calculated using the homogeneous electron gas functional.
- By LDA we can find lattice constants, bulk moduli, vibrational spectra, structure factor and much more.
- LDA also works well because error in the approximation of exchange and correlation tend to cancel.
- Exchange energy for LDA approximation is given as:

$$E_{xc} = \int n(r) \in_{xc} \mathrm{dr} \quad , \in_{xc} = \text{exchange correlation energy} \quad \textbf{-(6)}$$

1.2.3.3. Generalized Gradient Approximation

- The term generalized gradient expansion (GGA) denotes a variety of ways proposed for functions that modify the behavior at large gradient in such a way as to preserve desired properties.
- GGA functions are used in quantitative calculations, especially in chemistry.
- The exchange energy in GGA is a function of gradient of density.
- The exchange energy in GGA approximation is given by:

$E_{xc} = \int n(r) \in_{xc} (\mathrm{n}, \Delta r)\mathrm{dr}$ **-(7)**

1.2.3.4. The Pseudopotential Approximation

- In a metal the conduction electrons tend to move in a region of minimum ionic potential and their accumulation form which must balance the ionic charge to satisfy charge neutrality requirements of the metal. The net effective interaction experienced by an electron is quite small and it is known as pseudo potential.
- Pseudopotential do not have core eigen states.
- Pseudopotential present accurately predicts a simplified way of solving schrodinger equation and to energy eigen values of states.
- Ultra-soft pseudopotentialis are used in all cases whereas norm-conserving pseudopotentialis are used in elements like C, N, O, and F.
- There are many ready to use pseudopotential tables around, but there is not a single standard pseudopotential file format. Each code has its own format.
- QUANTUM EXPRESSO accepts an XML-like format called UPF, plus some old formats.
- The conditional probability of n(r), which is based on the form of potential used is shown for different cases in Fig. 4, given below:

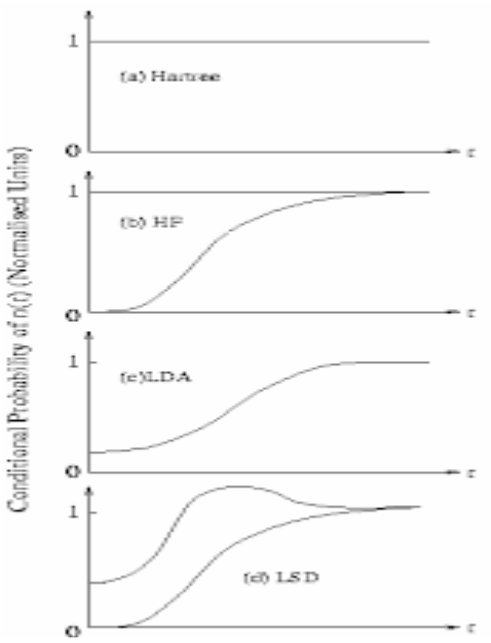


Fig. 4: Comparison of conditional probability of n® functions in

(a) Hartree Approximation;
(b) HF Approximation;
(c) DFT in Local Density Approximation(LDA);
(d) DFT in Local Spin Density Approximation (LSD).

2. Review of Literature

- Meng *et al.* (2019) reported a controllable method to synthesize two different morphologies of two dimensional (2D) 1T′-$MoTe_2$ film: rectangular $MoTe_2$ and irregular $MoTe_2$, respectively. The synthesis was carried out via chemical vapor deposition (CVD) with sodium chloride (NaCl) as promoters. Our results show that topography of rectangular $MoTe_2$ nanosheets have more uniform thickness while irregular nanosheets have poorer crystallization quality with more grain boundaries. Moreover, the surface friction decreases with the increasing thickness of 2D $MoTe_2$, owing to the gradually decreased surface corrugation of nanosheets as the thickness increase. This work provides a feasible method to synthesize the challenging transition-metal dichalcogenides (TMDs).
- Jia *et al.* (2018) reported that $TiSe_2$ thin films can be epitaxially grown on TiO_2 substrates despite different lattice symmetry between the two materials. The $TiSe_2$ thin films can be prepared on TiO_2 via molecular beam epitaxy (MBE) in two ways by conventional co-deposition using selenium and titanium sources, and by evaporating just selenium on reconstructed surfaces of TiO_2. Both growth methods yield crystalline thin films with similar electronic band structures. $TiSe_2$ films on TiO_2 substrates exhibit large electron doping and a lack of charge density wave (CDW) order, which is different from both bulk single crystal $TiSe_2$ and $TiSe_2$ thin films on graphene. These phenomena can be explained by selenium vacancies in the $TiSe_2$ films, which naturally occur when these films are grown on TiO_2 substrates. The successful growth of transition metal dichalcogenide (TMDC) films on a transition metal oxide (TMO) substrate provides a platform to further tune the electrical and optical properties of TMDC thin films.
- Walsh *et al.* (2017) studied the growth of WTe_2 thin films by molecular beam epitaxy which is demonstrated for the first time on a variety of 2D substrates including MoS_2, Bi_2Te_3, and graphite. They demonstrated that beam interruption of the metal source enables the growth of crystalline WTe_2 films in the distorted octahedral (1T′) phase. As a result of the van der Waals nature of this material, a sharp interface between the WTe_2 thin film and the substrate is shown with no evidence of misfit dislocations. In

addition, the buckled structure expected for the semi-metallic 1T′ phase is observed with transmission electron microscopy. Raman spectroscopy further confirms the growth of the 1T′ phase and x-ray photoelectron spectroscopy shows the films to be stoichiometric and semi-metallic as expected.

- Li *et al.* (2016) made detailed investigations of two-dimensional B_xN_y nanomaterials in the Cairo pentagonal tiling geometry fully composed of pentagons (penta-B_xN_y). Only penta-BN and BN_2 planar structures were found to be dynamically stable without imaginary modes in their phonon spectra. Their stabilities have been further evaluated by formation energy analysis, first-principles molecular dynamics simulation, and mechanical stability analysis. It was observed that Penta-BN_2 is superior to penta-BN in structural stability. Its stability analysis against oxidization and functional group adsorption as well as its synthesizing reaction path analysis show possibilities of fabricating penta-BN_2 in experiment. Furthermore, the penta-BN_2 could be transferred from metallic to semiconducting by ionizing or covalently binding an electron per dinitrogen. Also, it has been found to have superior mechanical properties, such as the negative Poisson's ratio and the comparable stiffness as that of hexagonal h-BN sheet. These studies on the stability, electronic properties, and mechanical properties suggest penta-BN_2 as an attractive material to call for further studies on both theory and experiment.
- Fadil *et al.* (2016) studied optoelectronic applications, of which two-dimensional materials such as molybdenum disulfide (MoS_2) are very promising candidates with their interesting electronic and optical properties. The layered structure of these materials makes them amenable to mechanical exfoliation to form scalable 2D atomic crystals. For wide range of applications, liquid phase exfoliation using sonication and centrifugation in appropriate solvent is needed. This simple and scalable technique gives high quality of exfoliation of 2D materials without chemical reactions. In this paper, the authors reported an example of the optical and electronic characterizations on MoS_2 synthesized by liquid exfoliation in specific solvent.

- Li *et al.*(2016) studied the latest research on material properties, device physics, fabrications and applications of two dimensional (2D) based materials including boron nitrides, black phosphorous and transition metal dichalcogenides/oxides beyond graphene. It features a balance between original theoretical and experimental research in basic physics, device physics, novel materials and device structures, processes and systems. They observed that the recent developments in the isolation and growth of atomically thin layered materials have provided new possibilities for studying the surfaces, chemistry and physics of a true 2D platform. In addition to the known graphene layers, other 2D materials such as transition metal dichalcogenides/oxides, boron nitride and black phosphorous have shown great potential in various applications. The 2D nature of these materials makes their electronic structure easily tunable to an external field. Thus, applications in electronic, optoelectronic, sensor and other devices are anticipated. The large surface areas and layered structures land to high-efficiency energy storage and conversion.
- Das *et al.* (2015) studied 2D materials and van der Waals solids and observed that such studies are growing exponentially across various scientific and engineering disciplines owing to their fascinating electrical, optical, chemical, and thermal properties. Whereas the micromechanical exfoliation technique has been adopted for rapid material characterization and demonstration of innovative device ideas based on these 2D systems, significant advances have recently been made in large-scale homogeneous and heterogeneous growth of these materials. The review reflects recent progress and outlines future prospects of these novel 2D materials. They provided a holistic overview of the different synthesis and characterization techniques, electronic and photonic device characteristics, and catalytic properties of transition metal dichalcogenides and their heterostructures.
- Xu *et al.* (2013) studied that derived from its 2D honeycomb shape, graphene has unique electronic, optical, mechanical, thermal, and chemical properties. Not only have the fundamental properties of graphene been discovered, but many interesting applications of graphene have also been demonstrated. However, to date, there has been no practical method for the large-scale and scalable production of graphene sheets with fine control over

the number and the structure of the layers over an entire substrate. A technique for the transferring of large-scale graphene sheets also needs to be developed. Low-temperature synthesis and catalyst-free synthesis are highly desirable for practical applications. In principle, graphene could be considered as a prototypical material used to investigate the fundamental physics and chemistry of other 2D systems and to explore their applications. The subject of grapheme like 2D crystals is now one of the most active fields of research in materials science, condensed matter physics, and chemistry, and is developing at a rapid pace. Although these 2D systems have been studied for only a couple of years, the findings thus far indicate that these 2D materials either exhibit electronic properties that are strikingly different from graphene or have properties that are similar to graphene. We also know that the physical and chemical properties of these 2D crystals can be modified by chemical doping, by application of strain, by intercalation with different types of atoms and molecules, and by application of electric fields. Together with graphene or the many alternatives to graphene, there is no doubt that these 2D materials with large specific surface areas and versatile and superb electronic and optical properties will soon be potentially useful for an enormous range of applications.

- Ma *et al.* (2011) studied two-dimensional nanosheets of $MoSe_2$, $MoTe_2$ and WS_2 which were successfully synthesized by them experimentally. In this work, the electronic and magnetic properties of perfect, vacancy-doped, and nonmetal element (H, B, C, N, O, and F) adsorbed $MoSe_2$, $MoTe_2$ and WS_2 monolayers were systematically investigated by means of first-principles calculations to give a detailed understanding of these materials. It was found that: (1) $MoSe_2$, $MoTe_2$ and WS_2 exhibit surprising confinement-induced indirect-direct-gap crossover; (2) among all the neutral native vacancies of $MoSe_2$, $MoTe_2$ and WS_2 monolayers, only the Mo vacancy in $MoSe_2$ can induce spin-polarization and long-range antiferromagnetic coupling;(3) adsorption of nonmetal elements on the surface of $MoSe_2$, $MoTe_2$ and WS_2 nanosheets can induce a local magnetic moment; H-absorbed WS_2, $MoSe_2$, and $MoTe_2$ monolayers and F-adsorbed WS_2 and $MoSe_2$ monolayers show long-range antiferromagnetic coupling between local moments even when their distance is as long as 12A˚. These findings were a useful addition to the experimental studies of these new synthesized two-dimensional nanosheets,

and suggest a new route to facilitate the design of spintronic devices for complementing graphene.

- Ghosh *et al.* (1996) studied a reentrant peak effect, observed through low field ac susceptibility measurements on the weakly pinned flux line lattice in single crystal of 2H-$NbSe_2$. The resulting phase diagram of the peak effect was strikingly similar to the theoretically predicted reentrant phase boundary which separates flux lattice and flux liquid phases. The broadening and ultimate disappearance of the peak effect at very low fields was found to be consistent with the predicted crossover to a disordered glassy state in this field regime.
- Zanin *et al.* (2004) studied the structure of Zn_3P_2 ($P4_2/nmc$, a = b = 8.0785 Å, c=11.3966 Å), was solved and refined to R = 3.2% in a precision X-ray diffraction experiment (λ-MoK_α, graphite monochromator on a primary beam, 27,496 reflections). Interatomic distances and bond angles were determined. It was observed that the fcc lattice of the structure is built from phosphorus atoms, and the zinc atoms occupy 3/4 of all tetrahedral voids; the structure was described by two equivalent models, where 1/4 occupied (by zinc atoms) and 1/4 vacant voids change places. The zinc atoms that occupy the voids following the diamond principle do not change places.

2.1 Motivation of Research:

Graphene's layered structure has opened new prospects for the exploration of properties of other monolayer two-dimensional (2D) crystals. The emergence of these inorganic 2D atomic crystals beyond graphene promises a diverse spectrum of properties.

For example, **hexagonal-boron nitride (h-BN)**, a layered material closest in structure to graphene is an **insulator**, **while niobium selenide ($NbSe_2$)**, a transition metal dichalcogenide, is **metallic**, and monolayers of other transition metal dichalcogenides such as **molybdenum disulfide (MoS_2) and tungsten disulfide (WS_2)** are direct band gap **semiconductors**.

The rich spectrum of properties exhibited by these 2D layered material systems can potentially be engineered on-demand and creates exciting prospects for using such systems in device applications ranging from electronics, photonics, energy harvesting, flexible electronics, transparent electrodes, and sensing. While the

layered structure of these materials makes them amenable to mechanical exfoliation for quickly unveiling their novel properties and for fabricating proof-of-concept devices, an overview of the synthesis routes that can potentially enable scalable avenues for forming these 2D atomic crystals, is shown in Table 3 and Fig. 5 given below.

TABLE 3: Example layered materials and their general properties

Material	**Property (trends/remarks)**	**Band Gap(bulk)**	**Band Gap(Monolayer)**
Graphene		0 eV	0 eV
h-BN	Insulator	5.97 eV(Exp.)	6.07 eV(Exp.)
Group 4B: Ti,Hf,Zr	Semiconducting and insulating, diamagnetic		
Sulfides: TiS_2,HfS_2,ZrS_2		HfS_2 :1.96 eV (Exp.)	
Selenides: $TiSe_2$,$HfSe_2$,$ZrSe_2$	$TiSe_2$ (with Cu interaction) Superconducting		
Tellurides: $TiTe_2$,$HfTe_2$,$ZrTe_2$			
Group 5B: V,Nb,Ta	Metallic or semimetallic, superconducting, charge density wave; paramagnetic, antiferromagnetic, diamagnetic		
Sulfides: VS_2,NbS_2,TaS_2	NbS_2 metallic		
Selenides: VSe_2,$NbSe_2$,$TaSe_2$			
Tellurides: VTe_2,$NbTe_2$,$TaTe_2$			
Group 6B: Mo,W			
Sulfides: MoS_2,WS_2	Semiconducting	MoS_2:1.0-1.29 eV (indirect) WS_2: 1.35 eV (indirect)	MoS_2:1.9 eV (direct) WS_2: 2.1-1.8eV (direct)
Selenides: $MoSe_2$,WSe_2	Semiconducting		$MoSe_2$: 1.44 eV (direct)
Tellurides:	Tellurides are		$MoTe_2$: 1.07 eV

$MoTe_2$,WTe_2	semimetallic and/or diamagnetic	(direct)
Group 7B: Tc,Re		
Sulfides: TcS_2,ReS_2	ReS_2 metallic	
Selenides: $TcSe_2$,$ReSe_2$		
Tellurides: $TcTe_2$,$ReTe_2$		
Group 10B: Pd,Pt	Semiconducting and/or diamagnetic	
Sulfides: PdS_2,PtS_2		
Selenides: $PdSe_2$,$PtSe_2$		
Tellurides: $PdTe_2$,$PtTe_2$	Tellurides are metallic and paramagnetic. $PdTe_2$ is superconducting	

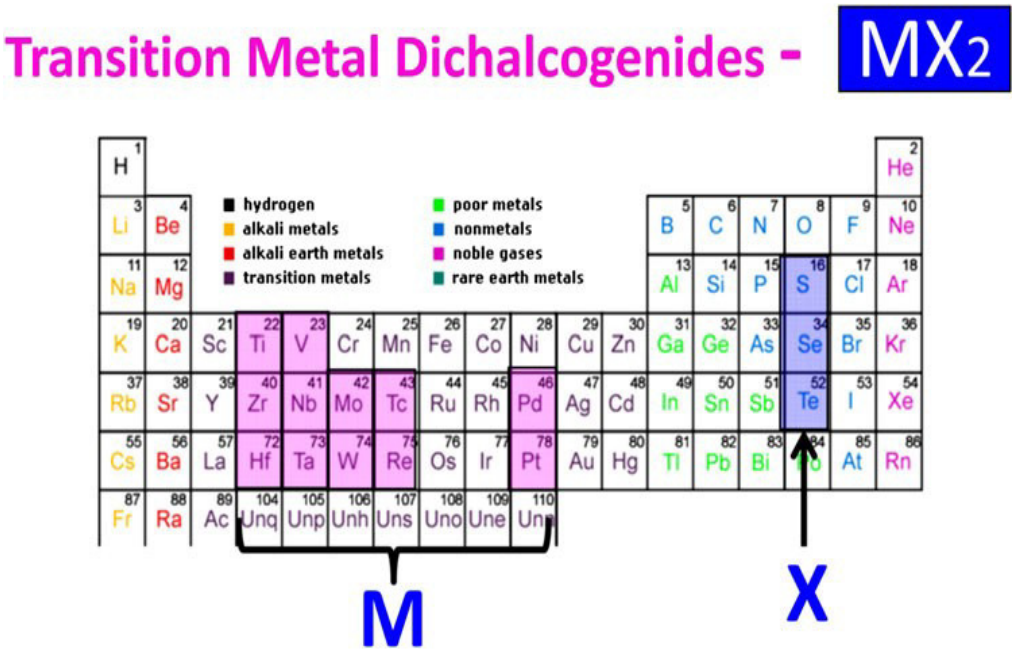


Fig. 5. The transition metal dichalcogenides are an example of 2D layered materials. Depending on the combination of the transition metal M and the chalcogen atom X (S, Se, and Te), a wide range of properties can arise.

2.2. Applications of layered materials

- *Electronics and optoelectronics:* Quantum dots, diodes, transistors, antennas, integrated circuits, photo-detectors, photovoltaic cells, light emitting devices, field emission devices.
- *Energy and Mechanics:* Thermoelectric devices, batteries, supercapacitors, fuel cells, solar panels, lubricants, traducers, Nano-electro-mechanical systems.
- *Materials:*Polymer and metal composites, functional and self-healing materials, aerospace composites, barrier coatings, corrosion protection, conductive inks, foams.
- *Chemistry and Physics:* Scaffolds for catalysis, membranes for filtration and desalination, sensors (gas, metals and environmental pollutants), radiation detectors, strain gauges, pressure, mass and temperature sensors, transducers.
- *Biology and Medicine:* Biosensors, biocompatibility, bio distribution, scaffold for tissue engineering, drug delivery, gene transfection, cancer therapy, diagnostic devices, etc.

3. Objectives of the proposed research work

1. To study electronic properties of some layered materials in 2D crystalline form (two materials of each type):

Conducing	Insulating	Semiconducting/ Semi-metallic
Graphene	**hBN**	**MoS_2 , $MoSe_2$, $MoTe_2$**
$NbTe_2$	**HfS_2**	**WS_2, WSe_2, WTe_2**
NbS_2	**Bi_2Te_3, Bi_2Se_3**	**$TiSe_2$**
Nb_3Cl_8	**Sb_2Te_3**	

2. To study electronic properties of above materials in bulk form and compare with the results obtained in 2D form.

3. To study the effect of doping with impurity on structural and electronic properties of 2D materials (in sample cases only).

4. To study structural properties of 2D materials and effect of pressure (in sample cases only).

5. To study effect of spin polarization on electronic structures of 2D materials (in sample cases only).

6. To study superconductivity of 2D materials (in sample cases only).

4. METHODOLOGY

The theoretical investigation of the above mentioned materials is proposed to be done by using software codes based on DFT. Some of the codes in use for electronic structure calculations of crystalline solids are:
ABINIT, CP2K, Dalton, SAMSON, WIEN2k, SIESTA, CRYSTAL, Quantum ESPRESSO, VASP, HORTON etc.
In the present research we propose to use WIEN2k and Quantum ESPRESSO, which are available in the University Computational Physics Lab. A small cluster of 5 nodes with server is also available to work with these codes.

For computations needing large RAM and memory requirements we propose to work at High performance computing system at IUAC New Delhi and other such facilities available elsewhere.

4.1 WIEN2k Software

4.1.1 Introduction

WIEN2k is a full-potential all-electron code developed by Blaha et al. at the Institut fur Materialchemie, Technical Universitat at Wien, Austria.

WIEN2k consists of many independent F90 programs, which are linked together via C-shell scripts. The code is based on the Kohn-sham formalism of DFT.
In order to solve Schrodinger equation, we have to construct the effective Hamiltonian operator which depends on the electron density of the electronic system. The manner through which the Schrodinger wave equation is solved within Code WIEN2k is represented by the flow chart shown below in Figure 6.

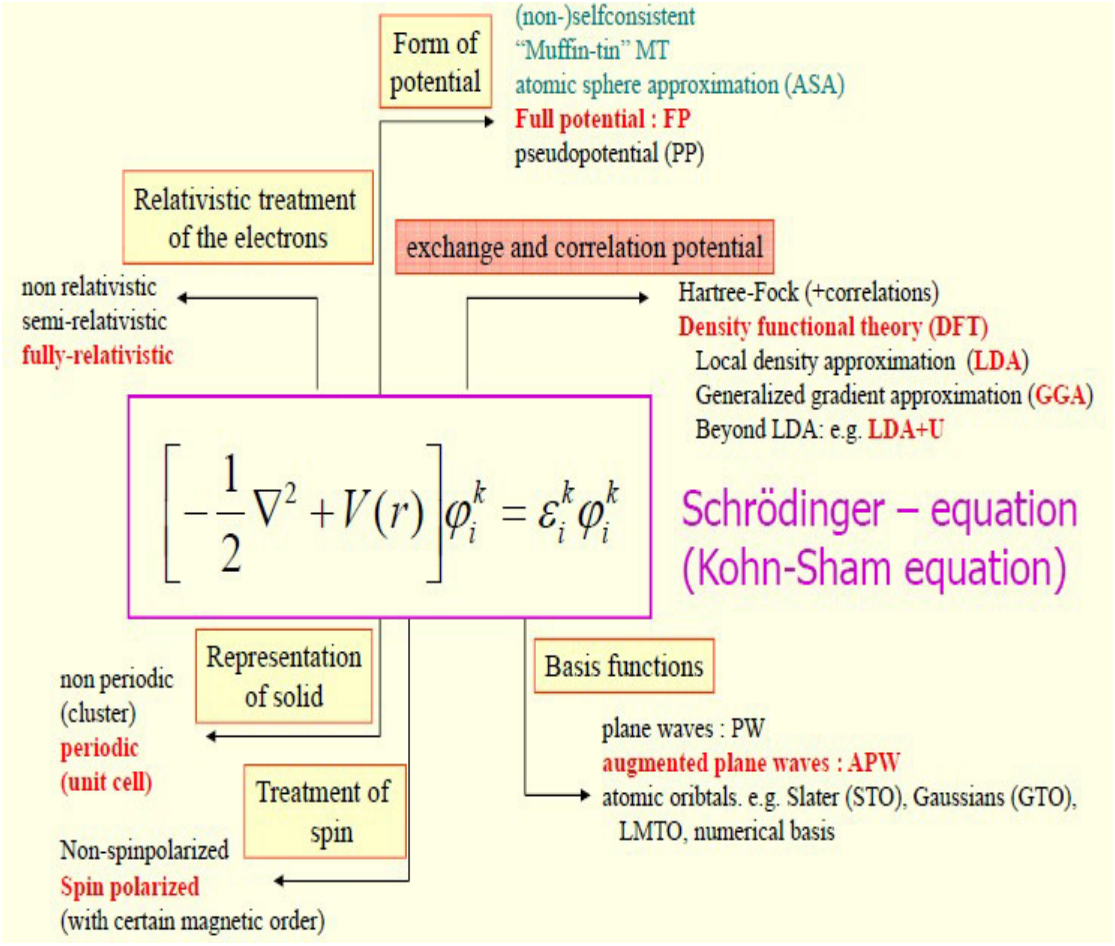


Fig. 6: Pictorial representation for the solution of Schrodinger equation, using WIEN2k and other codes based on DFT

4.1.2 Self Consistent Method

In order to obtain the ground state electron density; we solve Kohn-Sham equations are solved by using iterative method called Self consistent Field (SCF) method. Here, we use the atomic densities at the position of the atoms in the electronic system and set the Hamiltonian operator. From this, we derive the electron density in the system by solving Kohn-Sham equations and sum up the electron density of all the occupied states.

From the value of this new electron density, we can calculate a new potential and consequentially, new Hamiltonian operator. We now repeat this step as much as necessary to satisfy predefined convergence criteria on total energy of the crystalline material and sometimes also on electronic charge. The converged

result is then independent of starting potential and therefore self-consistent and good starting point to produce new electron densities.

4.1.3 Basis Function

To solve Kohn-Sham equations numerically besides the exchange correlation potential and full potential we must employ a set of basis functions in order to efficiently represent the electronic wave function. The electronic structure calculations done by first principles methods are employed by expanding the electronic wave function in basis sets of atomic orbital's.

4.1.3.1 Augmented Plane Wave Method

The wave function of Bloch vector k and band number λ is a linear combination of basis functions satisfying the Bloch boundary conditions. In periodic systems, an electronic wave function Ψ(r) can be written as a plane wave (PW). Plane waves constitute a complete and orthogonal basis set. Therefore, every electronic wave function can be written as,

$\Psi_{k\lambda}(r) = \sum_G C^{\lambda k} G$

Where, G are reciprocal lattice vectors, and C_G are variational coefficients. This works only for pseudo potentials and not for the potential with a singularity (1/r at the nucleus) i.e. for r=0 where strong fluctuations appear in the wave function close to the nucleus.

4.1.3.2 Linearized Augmented Plane Wave Method

In LAPW method, the weakly bonded electrons (e.g., valence electrons) are well described by PW which are the solutions to the Hamiltonian with a zero potential. On the other hand, a core electron (deep in energy) "feels" practically only the nucleus to which it is bonded and thus it is well described by spherical harmonics (solutions for a single free atom). The LAPW approach combines these two basis sets by setting up a muffin-tin (MT) sphere on each atom. The rest of the space is the interstitial region.
The LAPW method can be extended to non-spherical muffin-tin potentials with a little difficulty, because the basis offers enough variational freedom. This leads then to the full-potential linearized augmented plane wave method (FP- LAPW).

4.1.3.3 Full-Potential Linearized Augmented Plane Wave (FP-LAPW) Method

The accuracy of the LAPW + lo method can be further improved by using the full potential (FP). The potential approximated to be spherically symmetric inside the muffin-tins, while in the interstitial region the potential is set to be constant. It is a method used to simulate the electronic properties of materials on the basis of DFT. This method has been successfully applied to study structural phase transitions of certain semiconductors, which increases the number of plane waves in the basis set, in order to decrease the structural properties of systems accurately. The shape of the charge density is taken into account with high accuracy. In this method, the unit cell is divided into two regions as shown in Figure 7.

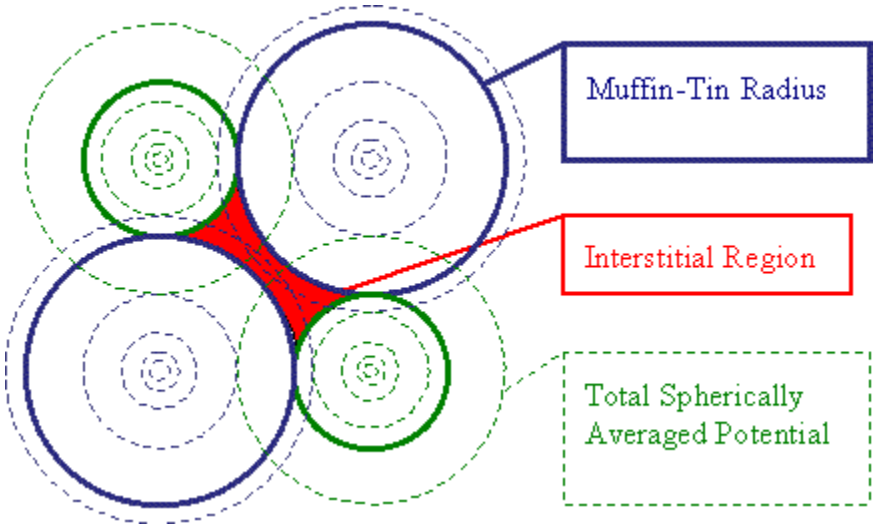


Fig. 7. The unit cell divided into muffin-tin region and interstitial region

In FP-LAPW method, both, the potential and charge density, are expanded into lattice harmonics inside each atomic sphere and as a Fourier series in the interstitial region.

$$V(r) = \begin{cases} \sum_G V_G e^{iG.r} & r \in IR \\ \sum_{lm} V_{lm}(r) Y_{lm}(\hat{r}) & r \in MT, \end{cases}$$

Therefore, the plane wave solves the Schrodinger equation in interstitial region, and the product of radial solution times the spherical harmonic solution solves the Schrodinger equation in the muffin-tin region.

4.1.4 Steps to Precede the Simulations Using WIEN2k

Generation of Structure

Each case runs in his own directory ./case

The master input is called case.struct

- Space group selection of the chosen material.
- Lattice parameters.
- Atomic positions in the unit cell.
- Selection of appropriately fitted Rmt's of atoms in unit cell structure.
- To import the cif file, for input

Initialization

The *case.struct* file for the material is initialized either by using the command *init_lapw* or through step by step process given below:

- Checking for atomic separations to be greater than sums of RMTs
- Detection of the symmetry.
- Generation of automatic input.
- Selection of k-points to be generated in irreducible wedge of first Brillouin Zone.
- Minimum separation energy required to stabilize the unit cell structure.
- Selection potential function.

During self-consistent functional, we have to make the appropriate selection regarding the nature of choose materials. For, a non-magnetic material there is no need to chosen the spin polarized option. In case the material is magnetic then following steps are necessarily considered.

- Spin-polarization.
- Spin - orbit coupling (strongly localized electronic system).
- Choice of diagonal matrix in strongly correlated systems.
- Electron and charge convergence limit.

SCF Calculations

This can be done by using the command
run_lapw (runsp_lapw)
or through GUI by specifying convergence limits for Energy and electronic charge.

The SCF calculation involves four steps, namely
LAPW0 (generates potential)
LAPW1 (generates eigenvalues and eigenfunctions)
LAPWSO (adds spin orbit coupling)
LAPW2 (generates valence charge density expansions)
SUMPARA (summation of files from parallel execution)
LAPWDM (calculate density matrix)
LCORE (generates core states)
Mixer (adding and mixing of charge densities)

After the successful completion of SCF, different properties of selected problems can be analyzed, like equilibrium lattice constants, bulk modulus, cohesive energy, electron density, band structure, density of states, optical response etc.
Some additional packages are also available for being used with this code, for example to analyze the elastic and thermal behavior of the materials under a wide range of pressure and temperature variations, PHON code for calculation of phonons etc.

4.1.5 Applications of code WIEN2K

The computer code WIEN2k is used to study crystal properties on the atomic scale by employing LAPW method within DFT, the most precise schemes for solving the KS equations. The advantage of first principle methods lies in the fact that they can be carried out without knowing any experimental data. In WIEN2k the alternative basis set (APW+lo) is used inside the atomic spheres for chemically important orbitals, whereas LAPW is used for others.
The problems considered so far in quantum mechanics using the LAPW method employed in various versions of the code WIEN2k, have covered a wide spectrum, including in particular insulators, semiconductors, metals up to f- electron systems and also intermetallics compounds. A brief description of applications of WIEN2k is as follows:

4.1.5.1 Structural Optimization

In cases where the atoms occupy general positions that are not fixed by the crystal symmetry, the knowledge of the forces acting on the atoms helps to optimize the structure parameters. Forces can be computed in WIEN2k and are crucial for such optimizations. The muffin tin radius (R_{mt}) of the atoms is also optimized as a function of energy of cell volume. The convergence of this basis set is controlled by a cutoff parameter $R_{mt}K_{max}$ = 6 - 9, where R_{mt} is the smallest atomic sphere radius in a unit cell and K_{max} is the magnitude of the largest K vector. If the smallest muffin tin radius is increased, the closest point a plane wave can come to a nucleus, moves farther away from the nucleus.

4.1.5.2 K Points Optimization

The output of a SCF run gives the physically relevant Hamiltonian operator as defined by the SCF charge density. The knowledge of the Hamiltonian operator allows us to extract the one particle energies and wave functions for any set of k-points. The k-point set consists of points along paths between high symmetry points in the first BZ. The k-point meshes for Brillouin zone sampling are constructed by Monkhorst-Pack scheme. The numbers of k-points are varied with respect to total electronic energy to ensure the convergence of k-points.

4.1.5.3 Equilibrium Volume and Bulk Modulus

The total energy (E) may be calculated by self-consistent run and hence expressed as the sum of Kinetic energy of electrons, Hartree energy, XC energy, Ion- electron interaction energy, Ion-ion interactions energy. The lattice constant of a solid corresponds to the size of the conventional unit cell length at the equilibrium volume and is obtained computationally by minimizing the total energy as a function of cell volume. Total energy for various lattice constants may be computed to obtain the value of lattice constant for which the total energy becomes minimal. This gives the equilibrium values of lattice constants. The results thus obtained can be fitted to Murnaghan's equation of state, to yield minimum energy volume and Bulk modulus of the system.

4.1.5.4 Total Energy and Phase transitions

The relative stability of different phases can be investigated by computing the total energy of such phases. With the knowledge of total energy, the relative stability of different phases can be computed by keeping as many parameters constant as possible, in order to have a cancellation of systematic errors. These parameters, for example, are: the atomic size of spheres, the plane-wave cut-off, the k-mesh, the DFT functional the treatment of relativity, etc. Because the energy differences are small, so a consistent treatment of the systems to be compared will help to minimize these computational effects.
The phase transitions from one crystal structure to other are determined by calculating the enthalpy in each case on inducing the effect of pressure. Total enthalpy in each crystal lattice is plotted against the range of pressure generated in correspondence of cell volume. The slope in energy versus cell volume curve also gives the complete information about high pressure phase transition.

4.1.5.5 Band Structure and Density of States (DOS)

The energy band structure and corresponding density of states are prominent quantities that determine the electronic structure of a system. Their inspection provides information about the electric property (metal, insulator or semiconductor) and gives insight into the chemical bonding.
The electron density is the key quantity in DFT. By taking its Fourier transform the static structure factors can be determined easily, and it can be compared with the experimental results.
An analysis of the crystal electronic structure permits direct insight and interpretation of experimental data (e.g., photoemission spectra) and determination of the material properties (optical, electrical, mechanical, magnetic and so on). It allows not only explains and interprets experimental results but is also the first step to predict and suggest ways for creating tailor made materials. Furthermore, a detailed understanding of the bulk properties is a necessary condition for a better understanding of more complex phenomena such as surface physics / Surface chemistry,etc.
The electronic structure calculations for solids can be done by this code using DFT. WIEN2k is one of the most popular electronic structure codes used to perform calculations with the FP-LAPW method. Also, it is one among the most accurate schemes for BS calculations. It is based on the full-potential (linearized) augmented plane-wave ((L) APW) + local orbitals (lo) method, one of the most accurate schemes for band structure (BS) calculations. An optimized geometry obtained through a self-consistent process is used to investigate the electronic

structure of the crystal lattice of a material. It may be pointed out that L(S) DA and GGA functional are not sufficient to give the complete view of electronic states in strongly localized orbitals. Hence the U parameters should be added during the SCF run.

4.1.5.6 Magnetic Properties

Magnetic properties of the materials show their behavior of response towards diamagnetic, paramagnetic, ferromagnetic or ferrimagnetic nature. Using spin-polarised BS calculations magnetic properties of these materials are studied. After calculating the total energy of the system corresponding to the equilibrium lattice volume, the magnetic moments are calculated by analyzing the case. Scfm file.
The values of magnetic moments are related to the number of atoms, interstitial sites and total magnetic moments are given individually.

The fixed spin magnetic moment (FSM) method implemented into the augmented spherical wave (ASW) scheme is used to analyze the magnetic moments as a function of total energy.
To calculate the properties of magnetic systems we need to extend the LAPW. This study of magnetic behavior utilizes a rotated spinors basis set inside atomic spheres and the pure spinors inside the interstitial sites. For heavier elements and strongly correlated systems, both the atomic moment approximation and inclusion of spin–orbit coupling (SOC) as well as Hubbard U correction should be involved.

4.1.5.7 Thermal Properties

Lattice dynamics is an important aspect to study properties of materials. It concerns with the vibrations of the atoms about their mean position. These vibrations are entirely responsible for thermal properties viz. heat capacity, thermal expansion, entropy etc. As the temperature and pressure of the material vary, it affects the density of the material which indicates the thermal expansion / contraction within the material leading to important and interesting results.
The amount of energy given to lattice vibrations in the crystalline solids is the dominant contribution to the specific heat which is a measure of degrees of freedom to absorb energy. The increased value in heat capacity may be correlated to the fact that the large value of the magnetic moments corresponding to the higher value of temperature becomes ordered.
Hence, in the present work several many properties using WIEN2k are proposed to be investigated for a large variety of structures, such as structural stability, high pressure phases, phase transitions etc. The roles of spin and orbital magnetic

moments, magnetic ordering (Para- or Ferro- magnetic) are also proposed to be one or two investigated in intermetallic compounds. LAPW calculations have helped to understand the structural, electronic, thermal and magnetic behavior of the solids. Super cells are also generated to enlarge the unit cells in all the three dimensions. In the present work, hypothetical or artificial structures are proposed to be considered by constructing supercells and introduce impurity atoms and their properties are calculated, irrespective of whether they can be exist in reality or not. Such calculations can predict the property of system i.e. either metal, insulator or semiconductor or find its magnetic structure. The changes in the systems under high pressure and temperature can also be simulated.

w2web GUI (graphical user interface):

The w2web is a powerful tool in WIEN2k,which is user friendly. The main components of w2web are:

- Structure generator
- Space group selection step by step initialization
  - symmetry detection
  - automatic input generation
- SCF calculations
  - Magnetism (spin-polarization)
  - Spin-orbit coupling
  - Forces (automatic geometry optimization)
- Guided Tasks
  - Energy band structure
  - DOS
  - Electron density
  - X-ray spectra
  - Optics

A Screenshot of structure file for WIEN2k is given below:

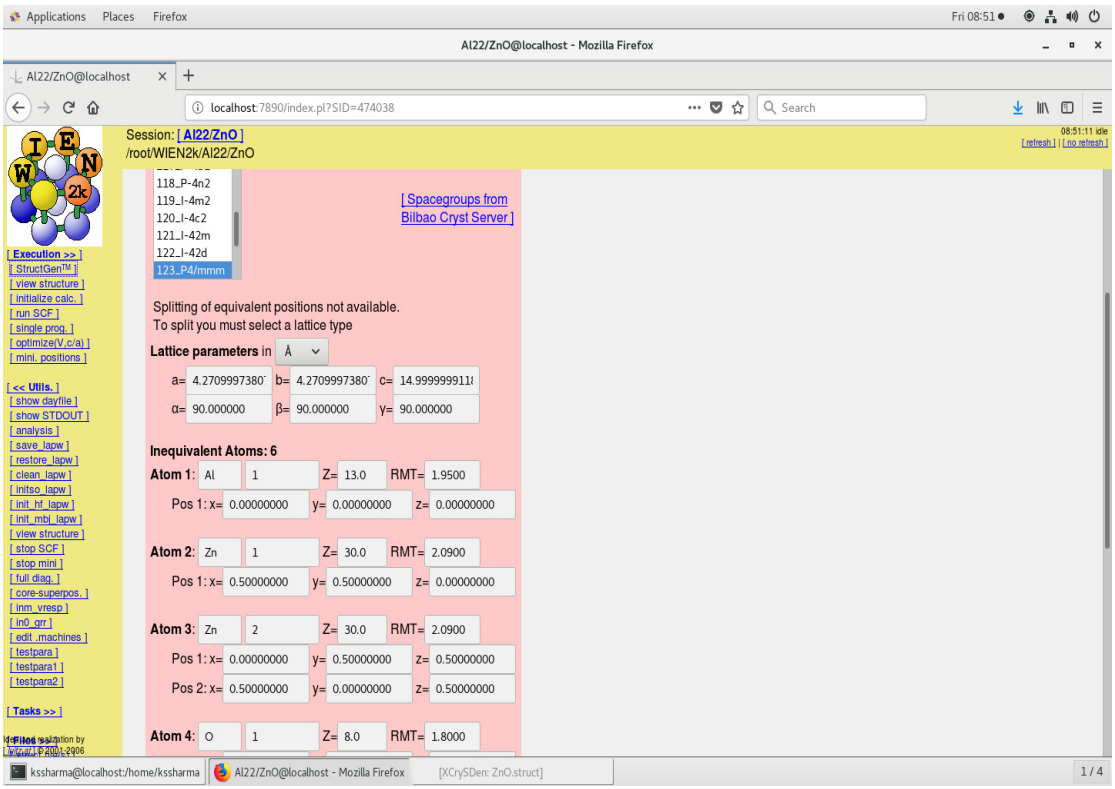


Fig. 8: A sample file screen for WIEN2k

Structure generator

To generate structure file, following information is to be provided for the material to be studied:

- Number of nonequivalent atoms
- lattice type (P, F, B, H, CXY, CXZ, CYZ) or spacegroup symbol
- lattice parameters a,b,c (in Ang or bohr)
- names of atoms (Zn) and fractional coordinates (position)
  1. As numbers (0.123); fractions (1/3); simple expressions (x-1/2,…)
  2. In fcc (bcc) specify just one atom, not the others in viz., (1/2,1/2,0; …)

Save structure – continue editing – save structure – save+cleanup

- W2web updates automatically Z, r, equivalent positions and generates case.inst

After „init_lapw / nn“ you know the distances between the atoms are displayed. *Go back to structgen and specify RMT:*

- non-overlapping “as large as possible” (saves time), but alongwith sums of RMTs should not be larger than 3 bohr

- RMT for sp-elements should be 10-20 % smaller than for d (f) elements
- Largest spheres should not be more than 50 % larger than smallest sphere
- Exception: H in C-H or O-H bonds: RMT~0.6 bohr (RKMAX~3-4)
- RMT in a "series" of calculations should not be changed.

Basic operations in WIEN2k :

init_lapw

- initialization
- symmetry detection (F, I, C-centering, inversion)
- input generation with recommended defaults
- quality (and computing time) depends on k-mesh and $R.K_{max}$ (determines #PW)

run_lapw

- scf-cycle
- optional with SO and/or LDA+U
- different convergence criteria (energy, charge, forces)

save_lapw tic_gga_100k_rk7_vol0

- cp case.struct and clmsum files,
- mv case.scf file
- rm case.broyd* files

4.2 Quantum ESPRESSO

Quantum *Op**E**n-**S**ource **P**ackage for **R**esearch in **E**lectronic **S**tructure, **S**imulation, and Optimization*, is a distribution (an integrated suite) of software for first-principle simulations, i.e., atomistic calculations based on electronic structure, using density-functional theory, a plane-wave basis set, pseudopotentials.

The main goals of Quantum ESPRESSO (QE) are

- Innovation in theoretical methods and numerical algorithms
- Efficiency on modern computer architect.

QUANTUM EXPRESSO PACKAGE

In QUANTUM EXPRESSO main components are:-

- *PWscf (Plane-Wave Self-Consistent Field):* This can be used to calculate total energy, phonon dispersion curve and molecular dynamics.

- *CP:* CP code is the specialization module performing Car-Parrinello ab initio in molecular dynamics. CP implements the same functional as PWscf with the exception of hybrid functions.
- *PHON:* It uses density functional perturbation theory for the calculation of second and third order derivatives of the energy. Advanced feature of this package is to calculate third order derivative of energy such as, electron-phonon and phonon-phonon interaction coefficient.
- *Atomic:*It is pseudopotential generate code. The atomic code uses the same exchange and correlation energy routines for PWscf.
- *GIPAW:* GIPAW codes allows for the calculation of:-
    1. NMR spectroscopy of an insulator.
    2. EPR spectroscopy for paramagnetic defects in solid.
- *XSPECTRA:* This code allows for the calculation of K-edge x-ray absorption spectra.

Organization

Website: *http://www.quantumespresso.org*

PWSCF code is used for quantum mechanical calculation of extended system. The PWSCF programme is part of the Quantum Espresso package.
PWSCF is an ab initio package that can perform density functional and Hartree-Fock calculations or the energy and electronic structure. It also can calculate various properties such as phonon dispersion curves, dielectric constant and born effective charges.

Method for Quantum Espresso

Login to the obtain software Linux and open the terminal.
For becoming super user type command *su* and provide password when asked.
This will take us to the home directory with # icon.
Then we change the directory to the Quantum Espresso directory by giving command.

Input File (Si) File:

```
&control
    calculation = 'scf'
    prefix = 'silicon',
    pseudo_dir = './',
```

```
    outdir = './'
/
&system
    ibrav = 2,                          #fcc lattice
    celldm(1) = 10.28,                  #lattice parameter
    nat = 2,
    ntyp = 1,
    ecutwfc = 25.0,
/
&electrons
/
ATOMIC_SPECIES
    Si 28.086 Si.pz-vbc.UPF
ATOMIC_POSITIONS alat                   #The atomic positions are specified in Cartesian coordinates, in
    Si 0.00 0.00 0.00                                units of the lattice parameter
    Si 0.25 0.25 0.25
K_POINTS automatic
4 4 4 1 1 1
```

5. WORK PLAN

Time duration	Work
0-6 months	**1) Collection of data for different materials to be studied.** **2) To understand usage of WIEN2K And Quantum ESPRESSO software**
6-12 months	**1) To study electronic properties of certain 2D materials and compare the same with the results of bulk materials .** **2) To study structural properties of 2D materials and effect of pressure (in sample cases only).** **3) To study effect of doping on electronic properties of certain 2D materials (in sample cases only).**
12-18 months	**1) To study effect of spin polarization on electronic structures of 2D materials (in sample cases only).** **2) To study superconductivity of 2D materials(in sample cases only).** **3) Publication of research papers in Journals.** **4) Presentation of results in conferences for their validation.**
18-24 months	**1) To carry out any remaining work.** **2) Preparation of thesis.** **3) Publication of research papers.** **4) Presentation of results in conferences**

6. BIBLIOGRAPHY

- Brown, B. E., and D. J. Beerntsen (1965). "Layer Structure Polytypism among Niobium and Tantalum Selenides." *Acta Crystallographica*, **vol. 18**, no. 1, pp. 31–36. doi:10.1107/S0365110X65000063.
- Kaul, Anupama B. "Two-Dimensional Layered Materials: Structure, Properties, and Prospects for Device Applications (2014)." *Journal of Materials Research*, **vol. 29**, no. 3, pp. 348–61.doi:10.1557/jmr.2014.6.
- Kepert, D. L., and R. E. Marshall (1974). "Electrical Properties of Metal Halides Containing Metal-Metal Bonds." *Journal of the Less Common Metals*, **vol. 34**, no. 1, pp. 153–63.doi:10.1016/0022-5088(74)90225-2.
- Meng, Yue, Ho-Kwang Mao, Peter J.Eng,Thomas P. Trainor, Matthew Newville, Michael Y.Hu, Chichang Kao, JinfuShu, Daniel Hausermann and Russel J. Hemley (2004). "The Formation of Sp^3 Bonding in Compressed BN." *Nature Materials*, **vol. 3**, no. 2, pp. 111–14. doi:10.1038/nmat1060.
- Novoselov, K. S., D. Jiang, F. Schedin, T.J. Booth, V.V. Khotkevich, S.V. Morozov, and A.K. Geim (2005). "Two-Dimensional Atomic Crystals." *Proceedings of the National Academy of Sciences*, **vol. 102**, no. 30, pp. 10451–53.doi:10.1073/pnas.0502848102.
- Radisavljevic, B., A. Radenovic, J. Brivio, V. Giacometti and A. Kis (2011). "Single-Layer MoS2 Transistors." *Nature Nanotechnology*, **vol. 6,** no. 3, pp. 147–50.doi:10.1038/nnano.2010.279.
- Schutte, W. J., J.L. De Boer, and F. Jellinek (1987). "Crystal Structures of Tungsten Disulfide and Diselenide." *Journal of Solid State Chemistry*, **vol. 70**, no. 2,pp. 207–09. doi:10.1016/0022-4596(87)90057-0.
- Solozhenko, V. L., G. Will, H. Hfipen and F. Elf (1994). "Isothermal Compression of Rhombohedral Boron Nitride up to 14 GPa." *Solid State Communications*, **vol. 90**, no. 1, pp. 65–67.doi:10.1016/0038-1098(94)90964-4.
- Stamov, I. G., Nicolae Syrbu and Dorogan Andrei (2013)."Energetic Band Structure of Zn_3P_2 Crystals." *Physica B: Condensed Matter*, **vol. 408**, pp. 29–33. doi:10.1016/j.physb.2012.09.029.
- Wildervanck, J. C., and F. Jellinek(1964). "Preparation and Crystallinity of Molybdenum and Tungsten Sulfides." *Zeitschrift Für Anorganische Und Allgemeine Chemie*, **vol. 328**, no. 5–6, pp. 309–18. doi:10.1002/zaac.19643280514.
- Yang, H. Y., T. Nummy, H. Li, S. Jaszewski, M. Abramchuk, D. S. Dessau and Fazel Tafti (2017). "Extreme Magnetoresistance in the Topologically Trivial Lanthanum Monopnictide LaAs." *Physical Review B*, **vol. 96**, no. 23,

p. 235128.doi:10.1103/PhysRevB.96.235128.

- Yang, Yi, Fei Gao, Shiwu Gao and Su-Huai Wei (2018). "Origin of the Stability of Two-Dimensional Perovskites: A First-Principles Study." *Journal of Materials Chemistry A*, **vol. 6**, no. 30, pp. 14949–55.doi:10.1039/C8TA01496E.
- Zhang, G. L., H. K. Yuan, H. Chen, A. L. Kuang, Y. Li, J. Z. Wang, and J. Chen (2014) . "Monoxides of Small Terbium Clusters: A Density Functional Theory Investigation." *The Journal of Chemical Physics*, **vol. 141**, no. 24, p. 244304.doi:10.1063/1.4904288.

7. REFERENCES

- Blaha, P., K. Schwarz, and P. Sorantin. "Full-Potential, Linearized Augmented Plane Wave Programs for Crystalline Systems (1990)." *Computer Physics Communications*, **vol. 59**, no. 2, pp. 399–415. doi:10.1016/0010-4655(90)90187-6.
- Fadil, Dalal, Ridwan H. Fayaz and Anupama B. Kaul (2016). "Electronic and Optical Properties Characterization of MoS_2 Two-Dimensional Exfoliated Nanomaterials." *MRS Advances*, **vol. 1**, no. 47, pp. 3223–28. doi:10.1557/adv.2016.523.
- Ghosh, K., S. Ramakrishnan, A. K. Grover, Gautam I. Menon, and Girish Chandra (1996). "Reentrant Peak Effect and Melting of a Flux Line Lattice in 2H-$NbSe_2$." *Physical Review Letters*, **vol. 76**, no. 24, pp. 4600–03. doi:10.1103/PhysRevLett.76.4600.
- Hohenberg, P., and W. Kohn(1964). "Inhomogeneous Electron Gas." *Physical Review*, **vol. 136**, no. 3B, pp. B864–71. doi:10.1103/PhysRev.136.B864.
- Jia, Tao, Slavko N. Rebec, Shujie Tang, Kejun Xu, Hafiz M. Sohail, Makoto Hashimoto, Dong-hui Lu, Robert G. Moore, and Zhi-Xun Shen (2018). "Epitaxial Growth of $TiSe_2$ /TiO_2 Heterostructure." *2D Materials*, **vol. 6**, no. ,1 p. 011008.doi:10.1088/2053-1583/aaeadf.
- Kohn, W., and L. J. Sham(1965). "Self-Consistent Equations Including Exchange and Correlation Effects." *Physical Review*, **vol. 140**, no. 4A, pp. A1133–38. doi:10.1103/PhysRev.140.A1133.
- Lee, C., X Wei, J W Kysar and J Hone(2008). "Measurement of the Elastic Properties and Intrinsic Strength of Monolayer Graphene." *Science*, **vol. 321**, no. 5887, pp. 385–88.doi:10.1126/science.1157996.
- Li, Lain-Jong, Daniel S P Lau, Stefan De Gandt and Fan Ren(2016). "Properties and Applications of 2-Dimensional Layered Materials." *ECS Journal of Solid State Science and Technology*, **vol. 5**, no. 11, pp. Y7–Y7. doi:10.1149/2.0181611jss.
- Li, Jiao, Xinyu Fan, Yanpei Wei and Gang Chen (2016). "Penta-B_xN_y Sheet: A Density Functional Theory Study of Two-Dimensional Material." *Scientific Reports*, **vol. 6**, no. 1, p. 31840.doi:10.1038/srep31840.
- Ma, Yandong, Ying Dai, MengGuo, Chengwang Niu, Jibao Lu and Baibiao Huang (2011). "Electronic and Magnetic Properties of Perfect, Vacancy-Doped, and Nonmetal Adsorbed $MoSe_2$, $MoTe_2$ and WS_2 Monolayers." *Physical Chemistry Chemical Physics*, **vol. 13**, no. 34, , p. 15546. doi:10.1039/c1cp21159e.

- Meng, Lan, Chaoji Xu, Heng Li, Xiangfu Wang and Xiaohong Yan (2019). "Controlled Synthesis and Frictional Properties of 2D $MoTe_2$ via Chemical Vapor Deposition." *Chemical Physics Letters*, **vol. 728**, pp. 156–59. doi:10.1016/j.cplett.2019.04.078.
- Walsh, Lee A., Ruoyu Yue1, Qingxiao Wang, Adam T Barton, Rafik Addou, Christopher M Smyth, Hui Zhu, Jiyoung Kim, Luigi Colombo, Moon J Ki1, Robert M Wallace and Christopher L Hinkle1 (2017)."WTe_2 Thin Films Grown by Beam-Interrupted Molecular Beam Epitaxy." *2D Materials*, **vol. 4**, no. 2, p. 025044.doi:10.1088/2053-1583/aa61e.
- Wang, Hong, Fucai Liu, Zheyu Fang, Wu Zhou and Zheng Liu(2014). "Two-Dimensional Heterostructures: Fabrication, Characterization, and Application." *Nanoscale*, **vol. 6**, no. 21, pp. 12250–72. doi:10.1039/C4NR03435J.
- Xu, Mingsheng, Tao Liang, Minmin Shi, and Hongzheng Chen (2013). "Graphene-Like Two-Dimensional Materials." *Chemical Reviews*, **vol. 113**, no. 5, pp. 3766–98. doi:10.1021/cr300263a.
- Zanin, I. E., K. B. Aleinikova, M.M.Afanasiev, and M. Yu. Antipin (2004). "Structure of Zn_3P_2." *Journal of Structural Chemistry*, **vol. 45**, no. 5, pp. 844–48. doi:10.1007/s10947-005-0067-9.
- Zeiss, G. D., and M. A. Whitehead(1983). "A Constrained Configuration Interaction Method." *Canadian Journal of Chemistry*, **vol. 61**, no. 11, pp. 2552–55. doi:10.1139/v83-439.